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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to ultrafine particle conductive paste suitable for especially formation of a 1.0 micrometer or less-thick thin conductor about the conductive paste used for formation of a laminated ceramic capacitor, the internal electrode of a multilayer ceramic board, etc.

[0002]

[Description of the Prior Art]In the electronics field, in order to manufacture parts, such as an electronic circuit, resistance and a capacitor, and an IC package, generally conductive paste, resistive paste, etc. which distributed conductive powder etc. are used into the organic vehicle.

[0003]These conductive paste and resistive paste conductive powder, such as metal, an alloy, and a metallic oxide, After carrying out mixture dispersion to an organic vehicle uniformly with a glassiness binding material and other additive agents if needed and applying this by methods, such as printing, on a substrate, a conductor tunic and a resistor tunic are formed by calcinating at an elevated temperature. As conductive metal powder used for conductive paste, base metals, such as the precious metals, such as Au, Ag, Pt, and Pd, nickel, Cu, Co, Fe, aluminum, Mo, W, or these alloys are used from fields, such as conductivity, stability, and cost.

[0004]In manufacture of laminated ceramic electronic components, such as a laminated ceramic capacitor (MLCC), the inner conductor layer inserted into the dielectric layer is formed by carrying out the plural laminates of uncalcinated a dielectric layer and a conductive paste layer by turns, and carrying out simultaneous calcination at an elevated temperature. As for the thickness of the dielectric layer in the present MLCC, and an inner conductor layer, it is supposed that 2.0-3.0 micrometers and an inner conductor layer are thin the dielectric layer to about 1.5 micrometers.

[0005]However, these days, small mass MLCC is demanded with a miniaturization and highly-efficient-izing of an electric product, information-and-telecommunications apparatus, etc. In order to attain big capacity by small volume, while raising the dielectric constant of a dielectric, it is desirable to make a dielectric layer and an inner conductor layer thin as much as possible, and to increase the number of laminations. Therefore, it is necessary to make still thinner thickness of a dielectric layer and an inner conductor layer, and development is furthered for the purpose of a thickness of 0.5 micrometer or less by 1.0 micrometer or less and an inner conductor layer by the dielectric layer, respectively.

[0006]

[Problem(s) to be Solved by the Invention]When forming a conductor film using conductive paste, if the particle diameter of solid content, such as conductive metal powder, is not or less at least 1 of the thickness of a target conductor film / 3, it is generally supposed that a flat and continuous conductor film cannot be formed. However, since the particle with a particle diameter of 0.4-1.0 micrometer is used as metal powder in the conductive paste for the present inner conductor layers, it is unsuitable for formation of a 1.0 micrometer or less-thick thin conductor film.

[0007]Although the method of forming a conductor film for having used the organic metal compound solution other than usual conductive paste is also developed, since the metal content in the solution is as low as 10-% of the weight order, only a 0.2 micrometer or less-thick thin film can be made. Since electrical resistance becomes large, such a thin film cannot be used as an inner conductor layer of laminated ceramic electronic components, such as a laminated ceramic capacitor (MLCC).

[0008]In forming a thin film on the semiconductor substrate which has the large contact hole and beer hall of an aspect ratio, the method of applying the dispersion liquid which made the organic solvent distribute the metal particles whose particle diameter is 0.001-0.1 micrometer is proposed by JP,9-134891,A. However, since this method cannot perform application of those other than a semiconductor substrate and also it has a fault, such as it being unsuitable for formation of an around 0.5-1.0-micrometer-thick conductor film, and being in it, it cannot be used for formation of the inner conductor layer of a laminated ceramic electronic component.

[0009]Once it takes out particles, such as metal powder, from a solution and dries them from the former after they are generated in a solution, it is used or marketed, but it is very easy to generate condensation of particles in this process, and some processing conditions cause powdered firm condensation. Since especially an ultrafine particle of 0.2 micrometer or less is very apt to condense particle diameter, it is actually made difficult to paste, and development of the art of distributing uniformly and pasting is desired, without making an ultrafine particle condense.

[0010]The conductive paste in which this invention distributed the ultrafine particle uniformly in view of such a conventional situation, It aims at providing an ultrafine particle ******-strike which was especially suitable for formation of the thin conductor film with a required as internal electrodes, such as a laminated ceramic capacitor and a multilayer ceramic board, thickness of 1.0 micrometer or less, and a manufacturing method for the same. It aims at providing the conductor film formed using this ultrafine particle conductive paste, and a laminated ceramic electronic component.

[0011]

[Means for Solving the Problem]In order to attain the above-mentioned purpose, ultrafine particle conductive paste which this invention provides is characterized by being an ultrafine particle whose particle diameter of total solids containing conductive metal powder is 1-300 nm, and content of this conductive metal powder being 10 to 80 % of the weight.

[0012]After a manufacturing method of the above-mentioned ultrafine particle conductive paste of this invention makes an ultrafine particle of conductive metal powder generate in a solvent with wet reduction, mixture dispersion of it is carried out to a vehicle, without separating an obtained ultrafine particle from this solvent.

[0013]This invention provides a laminated ceramic electronic component provided with a conductor film formed using the above-mentioned ultrafine particle conductive paste, and a conductor film formed using the

above-mentioned ultrafine particle conductive paste.

[0014]

[Embodiment of the Invention]The conductive metal powder in this invention contains after alloy powder and mixed metal powder besides single metal powder, and the ingredient consists of one sort or two sorts or more of elements selected from nickel, Co, Fe, Cu, Pb, Pd, Ag, Au, Pt, W, Mo, and aluminum. This conductive metal powder is an ultrafine particle with a particle diameter of 1-300 nm, and if particle diameter exceeds 300 nm, it will become difficult to form it of a 1.0 micrometer or less-thick conductor film.

[0015]Although the above-mentioned ultra-fine particle is compoundable by the gaseous phase method or any method of a liquid phase process, in order to suppress formation of the giant particle in which particle diameter exceeds 0.3 micrometer, its wet reduction using polyhydric alcohol, such as composition by wet reduction, for example, polyol etc., is more desirable than the large gaseous phase method of particle size distribution. Although the wet reduction by polyol has mainly been applied to composition of amorphous metal particles, when compounding a good crystalline ultra-fine particle, the speed of a reaction or crystal growth can be raised by a hydrothermal method. It is also effective in raising productive efficiency to compound applying microwave, an electric field, a magnetic field, an ultrasonic wave, etc. According to this method, crystallinity is good, the high-density metal of high dispersibility or the ultrafine particle of an alloy is obtained, and there is an advantage that particle diameter is uniformly easy also for that control.

[0016]In wet reduction, one sort or two sorts or more of inorganic matter, such as a nitrate, a chloride, sulfate, phosphate, an ammonium complex, carboxylate, metal alcoholate, and a resinate, or organic metal salt are used as a starting material compound of metal powder. If mixed use of two or more sorts of metal salt is carried out, after alloy powder and powder mixture can be obtained. As a reducing agent, polyol, hydrazine or its salts, polyvinylpyrrolidone, reducing sugar, hypophosphite, etc. are used.

[0017]What is necessary is for there to be no restriction in particular in the ingredient which constitutes a vehicle on the other hand, and just to adjust suitably resin and the solvent which are used as a binder of usual thick film paste according to the kind and use of a paste. For example, as a solvent, organic solvents, such as water, alcohols, ester species, acetone, ether, aromatic series, and hydrocarbon, or these partially aromatic solvents are used, and, as for resin used as a binder, cellulose, acrylics, and polyvinyl butyral are used. When manufacturing a paste, in order to distribute the above-mentioned ultra-fine particle easily, and to prevent the condensation and sedimentation of particles under storage moreover and to raise the preservability of a paste, to BIHIRUKU, a surface active agent, a dispersing agent, etc. can be added suitably.

[0018]In using it for a laminated ceramic capacitor (MLCC), the inner conductor layer of a multilayered ceramic substrate, or the outer-conductor film for simultaneous calcination, If the sintering start of metal powder is too early compared with ceramics when performing simultaneous calcination with a ceramic layer, it will be easy to generate the curvature of a structure defect like delamination or a crack, and a substrate, etc. by the disagreement of a sintering contraction action. In order to prevent this, the ultrafine particle or slurry of a dielectric, and the compound which generates an oxide at a suitable oxide ultrafine particle or elevated temperature are mixable into ultrafine particle conductive paste as a ** agent. Since sintering of an ultra-fine particle is controlled by this and the sintering start is overdue, laminated-structure defects, such as delamination and a crack, can be prevented. As for the particle diameter of a ** agent, what is still finer than it equivalent to an ultra-fine particle or is preferred.

[0019]In the ultrafine particle conductive paste of this invention, including the conductive metal powder of the above-mentioned ultrafine particle, the particle diameter of all the solid content is 1-300 nm, and let content of the conductive metal powder of an ultrafine particle be 10 to 80% of the weight of a range. If the particle diameter of solid content exceeds 300 nm, formation of a 1.0 micrometer or less-thick conductor film will become difficult, It is because the printing nature of a paste worsens and creation of a thin and **** coat is difficult, when a conductive conductor film with content of conductive metal powder good at less than 10 % of the weight cannot be formed but 80 % of the weight is exceeded conversely.

[0020]The ultrafine particle conductive paste of this invention does not have restriction in particular to a presentation in addition to the particle diameter of the above-mentioned solid content, and the content of conductive metal powder. Therefore, inorganic additives, such as other conductive powder, a ** agent, glass frit, a dispersing agent, and other organic additives may be made to contain if needed.

[0021]What is necessary is to double with the kind and use of a paste the conductive metal powder which consists of the above-mentioned ultrafine particle, BIHIRUKU, and other addition ingredients, and just to carry out dispersion mixing by the usual method, in order to adjust the ultrafine particle conductive paste of this invention. As the method of dispersion mixing, means, such as roll kneading, agitation mixing, dee ZUMIRU, and a ball mill, are used. When carrying out dispersion mixing by these methods, the particle diameter of the solid content under paste is eventually adjusted to the range of 1-300 nm.

[0022]Mixture dispersion of the ultra-fine particle is added and carried out to BIHIRUKU with a solvent, without separating an ultra-fine particle from a solvent thoroughly as an adjustment method of desirable ultrafine particle conductive paste, especially, after compounding an ultra-fine particle in a solvent with wet reduction. It can be made to distribute uniformly by this method, without an ultra-fine particle causing condensation. Actually, after evaporation, centrifugal separation, filtration, sedimentation, or other means remove most solvents, the remaining solvents and ultra-fine particles are mixed in a vehicle together with a ** agent, an additive agent, etc. Since the solvent used for wet reduction is mixed and pasted by the vehicle, without dissociating from an ultra-fine particle thoroughly, it is suitably chosen from water or an organic solvent according to the vehicle to be used.

[0023]What is necessary is just to calcinate formation of the conductor film by the ultrafine particle conductive paste of this invention, after applying or drawing in accordance with a conventional method since rheology characteristics, such as viscosity of a paste, can be adjusted by combination of the above-mentioned ingredient. For example, while being used by methods, such as printing, like usual thick film paste, since the solid content of a filler is an ultrafine particle, it is possible also for formation of a thin film, and the direct writing by a spray, dip coating, spin coating, or a micro dispenser is also possible for it.

[0024]Thus, by using the ultrafine particle conductive paste of this invention, 1.0 micrometer or less in thickness and also an about 0.5-micrometer thin conductor film can be formed easily without a defect. Therefore, the laminated ceramic electronic component which uses this thin conductor film as an internal electrode can be manufactured, and it is especially suitable for development and production of the small mass laminated ceramic capacitor (MLCC).

[0025]

[Example]Mixed ethylene glycol with example 1 nickel hydroxide by the weight ratio of 1:10, it was made to flow back for 10 hours, and the sol of nickel ultrafine particle whose particle diameter is about 20 nm was compounded.Then, after heating this sol and making a half grade condense ethylene glycol, the metal

content produced the conductive paste 50 % of the weight and whose resin content are 3 % of the weight by adding to the vehicle melted and made to terpineol, and carrying out agitation mixing of the ethyl cellulose uniformly beforehand.

[0026]This conductive paste assumed dark brown, the particle diameter of that nickel ultrafine particle was about 20 nm, and at ordinary temperature, even if it neglected it six months or more, separation was not seen. The pattern was formed on the alumina substrate by screen-stencil using this conductive paste, and after drying, the continuous nickel conductor film whose thickness with silver metallic luster is 0.9 micrometer was obtained by calcinating at 1000 ** in the reducing atmosphere containing hydrogen.

[0027]The sol of Au ultrafine particle whose particle diameter is about 30 nm was compounded by dissolving example 2 nitric-acid gold and polyvinylpyrrolidone (PVP) in dehydrated ethanol by the weight ratio of 1:10, and refluxing this mixed solution for 12 hours.Then, by adding to the vehicle melted and made to terpineol, and carrying out agitation mixing of the ethyl cellulose uniformly beforehand, after heating after repeating and washing this sol by ethanol, and making a half grade condense ethanol, The metal content produced the conductive paste 50 % of the weight and whose resin content are 3 % of the weight.

[0028]This conductive paste assumed the wine red color, the particle diameter of that Au ultrafine particle was about 30 nm, and at ordinary temperature, even if it neglected it six months or more, separation was not seen. After having formed the pattern on the alumina substrate by screen-stencil using this conductive paste, and drying, as a result of calcinating at 1000 ** in the air, the 0.8-micrometer-thick continuous golden conductor film was obtained.

[0029]It agitated having added this to terpineol with the dispersing agent, and applying an ultrasonic wave using Pd ultrafine particle whose mean particle diameter compounded by the example 3 gaseous-phase method is 0.1 micrometer, and was made to distribute uniformly.It kneaded with 3 rolls with the barium titanate ultrafine particle with a particle diameter of 0.1 micrometer which is the vehicle and ** agent which melted ethyl cellulose in terpineol beforehand and made these dispersion liquid, and the metal content produced the conductive paste 50 % of the weight and whose resin content are 3 % of the weight.

[0030]The particle diameter of the total solids which this conductive paste assumes a black color and contain that Pd ultrafine particle was about 300 nm or less. After having formed the pattern on the alumina substrate by screen-stencil using this conductive paste, and drying, as a result of calcinating at 1200 ** in the air, the 1.0-micrometer-thick continuous palladium conductor film was obtained.

[0031]Comparative example 1 Ni powder with a mean particle diameter of 0.6 micrometer marketed and the conductive paste containing about 10% of the weight of a ** agent,After having formed the pattern whose thickness of a wet state is 10 micrometers on the alumina substrate by screen-stencil, and drying, as a result of calcinating at 1000 ** in a reducing atmosphere, the 1.8-micrometer-thick continuous silver nickel conductor film was obtained.

[0032]Apart from this, when it thin-applied, the pattern whose thickness of a wet state is 5 micrometers was formed and it dried and calcinated like the above, the obtained conductor film became what has discontinuous island shape, and conductivity was not obtained.

[0033]After compounding the sol of nickel ultrafine particle from nickel hydroxide and ethylene glycol like the comparative example 2 above-mentioned example 1, the solvent was de**(ed) thoroughly and the end of nickel dried powder was obtained.It had the shape of a hard cake which assumed dark brown this end of dried powder, and when observed with the electron microscope, each particle formed firm floc. Although this

was ground and pasting was tried, particles could not be distributed but the flake of nickel was formed so much on the roll.

[0034]

[Effect of the Invention]According to this invention, the ultrafine particle conductive paste to which mixture dispersion of the conductive metal powder which consists of an ultrafine particle with a particle diameter of 1-300 nm was carried out uniformly can be provided, After compounding an ultra-fine particle with wet reduction including especially the polyol method, it can be considered as the ultrafine particle conductive paste distributed uniformly and stably without making an ultrafine particle condense by pasting a solvent, without dissociating thoroughly.

[0035]Since the ultrafine particle conductive paste of this invention is adjusted to the range whose particle diameter of total solids is 1-300 nm, it fits formation of the 1.0 micrometer or less-thick conductor film. It is suitable for formation of the conductor film of laminated ceramic electronic components, such as an especially small mass laminated ceramic capacitor (MLCC).

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